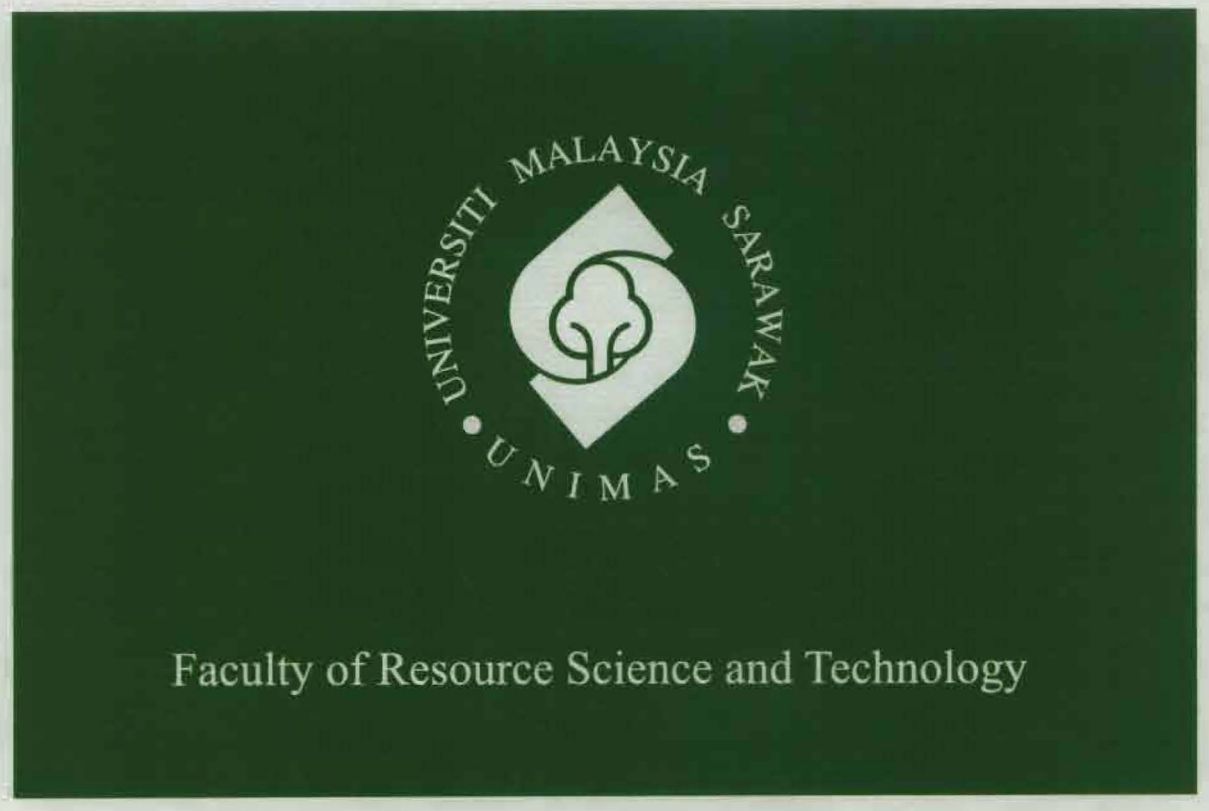

EFFECT OF REACTION TIME ON ACID HYDROLYSIS OF METHYL BENZOATE

NOR AZIMAH BINTI MORSALIN

(42813)

Bachelor of Science with Honours
(Resource Chemistry)
2016

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This project paper is submitted in partial fulfillment of requirements the Degree of Bachelor of Science with honors

(Program of Resource Chemistry)

Faculty of Resource Science and Technology

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2016

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Grade: A

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Final Year Project Report	✓
Masters	
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This declaration is made on the 17th May 2012.

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Acknowledgement

I have given hard works and efforts in this project. However, without the kind support and help of many individuals and organizations, this project is not possible to be done.

Firstly, I would like to express my sincere gratitude to my supervisor Miss Yusralina binti Yusof, for being a great mentor and encourages me for doing this project. Your support and advice on my project has been priceless.

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Besides, I owe my gratitude to all those people who directly or indirectly supported me through this project venture.

Table of Contents

List of Abbreviation

FTIR	Fourier Transform Infrared Spectroscopy
-H	Hydrogen group
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
KBr	Potassium manganate
NMR	Nuclear Magnetic Resonance
-OH	Alcohol group

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Abstract

Hydrolysis reaction was a common reaction that involves in the organic chemistry field in the presence of acid or base as the catalyst. Previous literatures have been reporting that the yield of hydrolysis product was continuously increased due to the increased of reaction time. In contrast, there was a literature that stated that the yield of hydrolysis product was started to decrease when it achieved its optimum reaction time. This study was focused on the effect of different reaction times (1 hour, 2 hours, 5 hours, 8 hours and 11 hours) on ester hydrolysis with constant concentration and temperature. Benzoic acid was produced from the acid hydrolysis by using methyl benzoate as the starting material. Two different strong organic acids which are hydrochloric and sulphuric acid were used as the catalysts. The effects of these catalysts were compared to determine their effects on the yield of benzoic acid. This study also determined the impact on the percentage yield of benzoic acid when the solvent such as methanol is used. The result obtained shows that the percentage yield was increasing when the reaction time increased. However, there was an optimum time for the hydrolysis reaction using HCl as a catalyst.

Keywords: *ester hydrolysis, catalyst, methyl benzoate, benzoic acid, reaction time*

Abstrak

Tindak balas hidrolisis adalah tindak balas biasa yang terlibat dalam bidang kimia organik dengan kehadiran asid atau alkali sebagai pemangkin. Kajian sebelum ini telah melaporkan bahawa hasil produk meningkat secara berterusan disebabkan oleh peningkatan tindak balas masa. Walaupun begitu, terdapat juga kajian yang melaporkan hasil produk mula menurun apabila ia mencapai masa tindak balas optimum. Oleh itu, kajian ini memberi tumpuan kepada kesan tindak balas pada masa yang berbeza (1 jam, 2 jam, 5 jam, 8 jam dan 11 jam) ke atas ester hidrolisis dengan kepekatan dan suhu tetap. Metil benzoat telah digunakan sebagai bahan permulaan justeru menghasilkan asid benzoik. Selain itu, kajian ini menggunakan dua asid organik yang berbeza sebagai pemangkin asid seperti asid hidroklorik dan asid sulfurik untuk membandingkan kesan pada hasil asid benzoik. Oleh itu, kajian ini juga mengkaji kesan ke atas hasil peratusan asid benzoik apabila pelarut seperti metanol digunakan.

Kata kunci: ester hidrolisis, pemangkin, metil benzoat, asid benzoik, tindak balas masa

1) Introduction

1.1 Background

The term hydrolysis is referred to a chemical transformation in which the bond of an organic molecule breaks in the presence of water molecule. Hydrolysis is a chemical process where the molecules are cleaved into two fragments after the addition of water. The excess of water give one fragment of the cleaved molecule a hydrogen ion (H^+) while the other fragment is accepting the remaining hydroxyl ion (OH^-) (Joseph, 2004).

Figure 1: Hydrolysis reaction

According to Larson and Wiber (1994), hydrolysis is an example of a larger class of nucleophilic substitution reaction. Nucleophilic substitution reaction is initiated by a nucleophile reacts with a substrate to replace a substituent that depart on an unshared electron pair. Nucleophilic reagent is an ion which has a negative charge for example OH^-, while electrophilic reagents comprised of positive charged ion such as H^+ (Cram & Hammond, 1964).

Under normal conditions, the reaction of an organic compound and water molecules rarely occur. This is because the water molecule is a weak nucleophile. Therefore, a strong acid or base is required to catalyse the reaction (Clark & Pazdernik, 2012).

An ester is hydrolysed either by aqueous base or by aqueous acid to yield a carboxylic acid together with alcohol (Loudon, 2002). Figure 1 shows the pathway of the

ester hydrolysis. In consequence, this study observed the effect of the percentage yield when the reaction time is increased.

According to Ovissipour *et al.* (2009), the hydrolysis of one compound is affected by the reaction time and temperature. This study stated that in order to obtain a high degree of hydrolysis, the longer time and high temperature of the hydrolysis process was needed. Furthermore, hydrolysis reaction might be influenced by several factors. For example; concentration, pH and temperature (Ciobotaru *et al.*, 2016). This study was aim to identify the effect of reaction time to the yield production of benzoic acid catalyst reaction.

The methyl benzoate or methyl benzene carboxylate has been used in this study as the starting material.

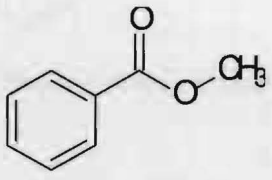

Figure 2: Methyl benzoate

Methyl benzoate (Figure 2) is an organic compound that contains an ester group (Leary & Marlier, 1978). It can be formed by condensation of methanol and benzoic acid. Methyl benzoate has a characteristic of colourless to slightly yellow liquid colour. Apart from that, this organic compound is immiscible in water and mostly soluble in organic solvent such as diethyl ether (Ege *et al.*, 1989). According to Kagaya and Yoshimori (2012), methyl benzoate's density is 1.08 g/ml which is greater than that of water. Therefore, this compound has been used as a non-halogenated extraction solvent for dispersive liquid-liquid microextraction (DLLME).

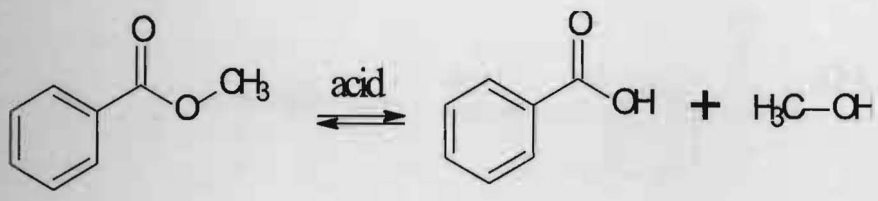

Figure 3: Equation of acid hydrolysis

Synthesis of benzoic acid (Figure 3) from acidic hydrolysis of methyl benzoate with high yield was the priority in this study. The benzoic acid is a compound that contain carboxylic group (Carey, 1992).

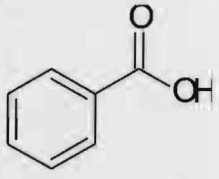

Figure 4: Structure of benzoic acid

Compound in Figure 4 exists as a white crystal solid and slightly soluble in water (Wibbertmann *et al.*, 2005). It can be produced by chemical synthesis but it also can be found from natural source, for example gum benzoin. Gum benzoin is the product that contains the benzoic acid component. This product can be extracted from the resin exuded by certain bark tree such as species of *Styrax* trees.

Ester can be hydrolysed to carboxylic acids under either acidic or basic condition (Hornback, 2006). Acidic hydrolysis of ester can occur by more than one mechanism, depending on the structure of the ester. Under acidic condition, the reaction is reversible. The reverse reaction of acid hydrolysis (Figure 5) is known as Fisher esterification reaction (Hornback, 2006).

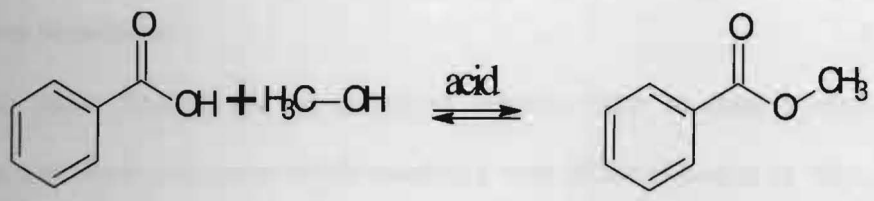

Figure 5: Equation of Fisher esterification

Ester is reacted with water molecule to undergo the nucleophilic addition reaction. Transfer of proton and elimination of alcohol yields the carboxylic acid.

1.2 Problem Statement

This study focused on the effect of reaction time in ester hydrolysis. This experiment was conducted under acidic condition with different period of time. Since the ester hydrolysis is important in many applications today, the optimum condition for doing this hydrolysis is being emphasized. According to Amenaghawon *et al.* (2014), the yield of the product increases due to the increase in reaction time. However, Herrera *et al.* (2003) reported that the product yield decreases when it achieved its optimum reaction time. Therefore, this study will identify on how the different duration influence the yield production of benzoic acid in acid hydrolysis.

1.3 Objective

The major objectives of this study are:

i) To determine the effect of time in acid hydrolysis of ester.

ii) To identify the duration that is optimum for ester hydrolysis reaction under acidic condition take place.

iii) Characterization and analysis of product by FTIR, NMR, and melting point.

2) Literature Review

2.1 Hydrolysis reaction

Hydrolysis reaction takes place in the presence of water. The presence of water molecule is important in order to perform the chemical transformation of an organic molecule such as an ester. The ester group was reacting with water molecule resulting in the displacement of leaving group -OR by OH^- (Larson & Weber, 1994). This statement has been supported by Bruice (2006), which stated that hydrolysis is a reaction that occur in the present of water to convert one compound into two compounds (Figure 1).

Furthermore, due to Clark and Pazdernik (2013), hydrolysis reaction is a process in which an organic molecule is cleaved into two parts in the addition of water molecule which one fragment of the parent organic molecule gains a hydrogen ion (H^+) whereas another one fragment attaches to the remaining hydroxyl group (OH^-). Larson and Weber (1994) reported that hydrolysis reaction referred to nucleophilic displacement reactions where a nucleophile atom attacks an electrophile atom. The most common hydrolysis occurs when a salt of a weak acid and/ or a weak base dissolves in water resulting in the breaking down of the salt into positive and negative ions (Clark & Pazdernik, 2012). Clark and Pazdernik (2012) stated that, under normal condition, strong acids or strong bases need to be added into the solution of water and organic compound to achieve the hydrolysis reaction. These acids or bases were considered as catalyst (Clark & Pazdernik, 2012).

2.2 Example of different types of hydrolysis reaction

2.2.1 Ester hydrolysis

Ester hydrolysis is the examples of hydrolysis reaction. This reaction occurs when ester is reacts with water molecules and they form carboxylic acid and alcohol (Bruice,

2006). Ball *et al.* (2011) also reported that ester hydrolysis reaction occurs when an ester compound is cleaved to two new components of carboxylic acid and alcohol (Figure 1).

According to Bruise (2006), hydrolysis reaction of an ester has been identified as a very slow reaction because water is a poor nucleophiles and ester has very basic (poor) leaving group. Acid hydrolysis which is the reverse of fisher esterification (Figure 5) occurs when the ester is heated with a large excess of water containing a strong acid catalyst (Ball *et al.*, 2011). In laboratory, a catalyst is usually used to enhance and speed up the reaction without being consumed or changed in the overall reaction. Thus, the slow step of the ester hydrolysis reaction between the ester and water might be faster. The formation of tetrahedral intermediate (Figure 7) will be faster by the presence of concentrated acid as the catalyst (Bruice, 2006).

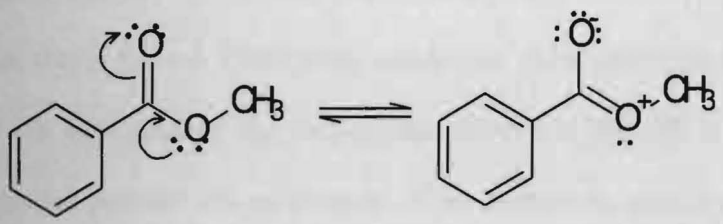

Figure 6: Protonation of carbonyl group

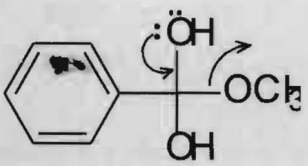

Figure 7: Tetrahedral intermediate in acid catalysed ester hydrolysis

2.2.2 Amide hydrolysis

Amides are very unreactive and are much less reactive than acid chlorides, acid anhydrides, or esters (Loudon, 2002). Bruice (2006), stated that since this compound is very unreactive, amides are usually found in the protein which imparts strength to biological structure. For example, the amide linkage is so stable that it serves as the basic unit from which protein are made. Due to McMurry (2012), amides are like ester which presence in abundant in all living organisms. Amide functional group can be found in proteins, nucleic acids and many pharmaceutical agents. However, amides can be hydrolysed with water and alcohols when the compound is heated with the presence of acid. Loudon (2002) also reported that hydrolysis of the amides often requires vigorous heating in either aqueous acid or base. The author stated that under acidic conditions, the equilibrium for the hydrolysis of amides driven towards the products by protonation of the ammonia or amine that is formed. Under basic conditions, the equilibrium is driven toward the products by the formation of the carboxylate anion and the pH is required to be adjusted to the desired product. As an example, if the carboxylic acid is produced as the product, thus, the final solution must be acidic.

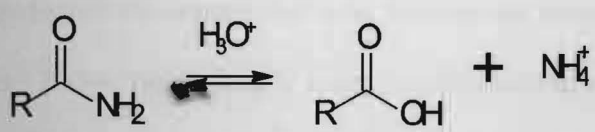

Figure 8: Equation of acidic hydrolysis of an amide.

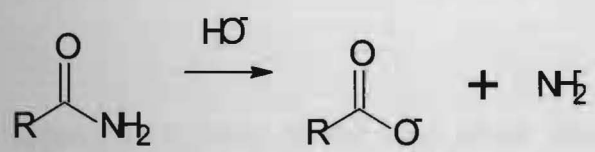

Figure 9: Equation of basic hydrolysis of an amide.

2.4 Effect of reaction time in hydrolysis reaction

The reaction time is one of the factors that influence the product of a reaction (Ciobotaru *et al.,* 2016). Due to Ciobotaru *et al.* (2016), hydrolysis reactions might depend on several factors such as concentration, pH and temperature. As an example, Akpinar *et al.* (2009) reported that the production of xylooligosaccharide is depends on both hydrolysis time and acid concentration. Al-Bahri *et al.* (2008) stated that in protein hydrolysis reaction, the effect of reaction time comes after the effect of both temperature and the concentration of the acid. Besides, this study found that reaction time is the only factor that gives the positive effect on the protein hydrolysis.

2.5 Methyl benzoate

Methyl benzoate is an organic compound that contains an ester group (Leary & Marlier, 1978). According to Dudavera *et al.* (2000), volatile ester methyl benzoate can be found in snapdragon flowers as the most abundant scent compound. The study reported that this compound is synthesized by and emitted from the upper and lower lobes of petals which the part of pollinators, for example bumblebees are attracted. Waggoner *et al.* (1997) reported that methyl benzoate is a consistent product of cocaine hydrochloride when it is exposed to humid air. Esters are among the most widespread of all naturally occurring compounds (McMurry, 2004). Many simple esters are pleasant-smelling liquids that are responsible for the fragrance odours of fruits and flowers (McMurry, 2004). Furthermore, the chemical industry uses esters for a variety of purposes. For example, ethyl acetate is commonly used as a solvent and dialkyl phthalates are used in polymer as plasticizers.

2.6 Benzoic acid

Benzoic acid appears as a white crystal solid which likely similar to needle appearance. This compound is the most simplest and familiar for the aromatic acid type (Bahl & Bahl, 2006). Benzoic acid compound can be found in gum benzoin which

extracted from the natural resource. Bahl and Bahl (2006) found that this compound also can be prepared by several methods. Firstly, by oxidation of toluene with air and Co-Mn acetate as the catalyst. Next, this compound also can be prepared by chlorinating toluene to benzotrichloride. Hydrolysing the latter by boiling with aqueous calcium chloride in the presence of iron powder as the catalyst also one of the ways to prepare the benzoic acid. Schwab and Wichers (1940) reported that benzoic acid also can be produced by hydrolysis of purified benzoyl chloride. These researches stated that the purification of this compound required either one of the method; distillation, fractional freezing and crystallization from solvent. Pavia *et al.* (1988) added that benzoic acid can be prepared by Grignard reaction.

Benzoic acid can be used in various types of applications, for example, in the pharmaceutical industry and dye industry (Bahl & Bahl, 2006). Apart from that, this compound also used as the preservative in food such as cheeses, varying sauces and ketchup as well as meats to keep them from spoiling as they eliminate the existence of yeast and bacteria. The antifungal properties of benzoic acid make this product suitable to be used by athletes to treat ringworm and also used to recover the irritation along with inflammation. However, due to Hill (2010), this chemical is dangerous to human health. The study stated that, the inhalation of this benzoic acid can lead to the damage of nervous system. Therefore, as the benzoic acid also used as the preservative in foods, eaten the food might resulted in a middle toxicity.

3) Methodology

3.1 Acid dilution

Preparation of 6M HCl

The volume of distilled water that was used to dilute 6M HCl was calculated by using the formula of $M_1V_1 = M_2V_2$

250 ml of distilled water was added to the 500 ml volumetric flask. Then, 250 ml of 12M HCl was poured into the distilled water. The solution was cooled down at room temperature.

Preparation of 6M H_2SO_4

The volume of distilled water that was used to dilute 6M HCl was calculated by using the formula of $M_1V_1 = M_2V_2$

333.33 ml of distilled water was added to the 500 ml volumetric flask. Then, 167.67 ml of 95-98% sulphuric acid was poured slowly into the distilled water. The solution was placed at room temperature to cool down.

3.2 Synthesis of benzoic acid

i) Acid hydrolysis (HCl as the catalyst) reaction without methanol.

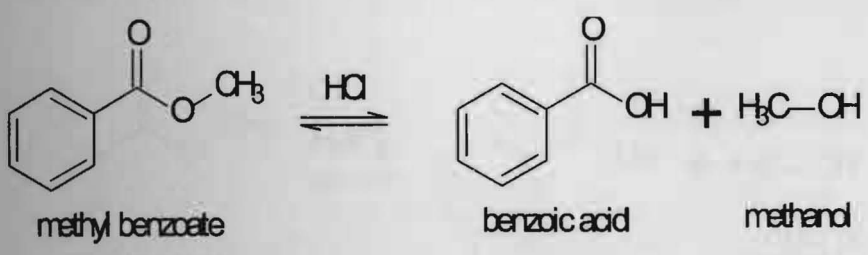

Figure 10: Equation of acid hydrolysis without methanol